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(54) Acrylic Acid Polymerization

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ACRYLIC ACID POLYMERIZATION

Background of the Invention

This invention relates to a process for homopolymerizing monoethylenically unsaturated C_3 to C_5 carboxylic acids and more specifically to homopolymerization in carbon dioxide.

It is well known in the art to produce polymers by dispersing the starting monomer in a liquid solvent. On f the major disadvantages of conventional liquid solvents is that they are relatively costly and generally must be removed from the final product. Accordingly, it is a purpose of the instant invention to provide a process f r polymerizing the above carboxylic acids which greatly facilitates the separation of the polymer from any solvents or reaction media.

The Journal of Organic Chemistry, 1984, vol. 49, pages 5097 to 5101, discloses the use of liquid and supercritical carbon dioxide as a solvent for various organic compounds. It includes a relatively long table illustrating solubilities of various organic compounds in liquid CO_2 and indicates that most of those that are soluble in liquid CO_2 are also soluble in supercritical carbon dioxid .

U.S. Patent 3,294,772 discloses polymerization of 1-olefins containing from 3 to 8 carbon atoms using the olefin itself as a solvent under supercritical conditions

and in the absence f any additional solvent. Polymerization is then followed by lowering the supercritical pressure while retaining the olefin in fluid form to precipitate only the crystalline portion of the olefin composition maintaining the non-crystalline portion in solution followed by fractionation.

U.S. Patent 4,250,331 discloses an extraction process using supercritical carbon dioxide by itself or with another supercritical gas to react with a salt of a carboxylic acid in aqueous medium to produce the carboxylic acid which separates from the aqueous phase and dissolves in the supercritical gas phase. In this patent, the carbon dioxide is used as a solvent but also as a reactant to convert a salt of a carboxylic acid to produce the organic acid itself.

Summary of the Invention

The instant invention is directed to a process for preparing homopolymers of C_3-C_5 monoethylenically unsaturated carboxylic acid preferably acrylic acid and methyacrylic acid, crotonic acid, alpha-methyl crotonic acid, alphaethylacrylic acid, dimethyl acrylic acid, alpha-chloro acrylic acid and vinyl lactic acid. As used throughout the instant specification and claims, excepting the examples, the expression "acrylic acid" includes methacrylic acid. This process comprises polymerizing the carboxylic acid in a

polymerization zone in fluid carbon dioxide in the presence of an initiator or catalyst.

In the following specification, the words "initiator" and "catalyst" are used interchangeably. Henceforth, only the word "initiator" will be employed.

In the following specification, the reaction is also disclosed as being carried out in fluid carbon dioxide, i.e. in carbon dioxide in a liquid or supercritical state. The invention as claimed hereinafter is however restricted to the process where the reaction is carried in carbon dioxide in a supercritical state, exclusively. This of course means that the reaction is carried out at a temperature and pressure at which the carbon dioxide is in such a supercritical state.

A supercritical fluid exists as a form of matter in which its liquid and gaseous states are indistinguishable from one another. The critical temperature of the fluid is the temperature above which that fluid cannot be liquefied by an increase in pressure. The critical pressure of a fluid is simply the pressure of the fluid at its critical temperature. Carbon dioxide is a supercritical fluid when its temperature exceeds 31°C and the pressure exceeds 73 atmospheres (about 1070 psi).

Fluid carbon dioxide has, the advantage as a reaction medium, that it is neither toxic nor flammable, is relatively inexpensive and may be removed from the polymer at low tempertures.

<u>Description of the Preferred Embodiments</u>

In accordance with a preferred embodiment of the instant invention the carboxylic acid is polymerized by charging the acid, liquid CO_2, and initiator to a high pressure reaction vessel and heating to initiate polymeriza- ______________________________

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tion. The mixture is allowed to react for a period of from about 0.25 to 5 hours depending on the rate of polymerization desired. It has been found that the instant process can be most practical in producing acrylic acid polymers having a molecular weight of from about 1000 to 1,000,000. At the end of the reaction period the pressure in the reaction vessel is reduced to atmospheric leaving a solid, water-soluble acrylic acid polymer and catalyst residue, the carbon dioxide going off as a gas. A preferred initiator is 2-t-butylazo-2-cyanobutane. Other preferred initiators are 2,2'-azobis-(2-methylbutyronitrile); t-butylhydroperoxide and benzylperoxide. Other initiators that may be employed are hydrogen peroxide, persulfates, benzyolperoxides, methyl ethyl ketone peroxide, perphthalic acid, and perbenzoic acid.

Liquid carbon dioxide may be obtained at temperatures as low as -55°C and pressures as low as 77 psi and there are possible ways to initiate polymerization at low temperatures such as the use of peroxide initiators. Preferably the minimum temperature is about -15°C and the minimum pressure is about 335 psi. Since the liquid carbon dioxide charged is often at very low temperatures it may be necessary in order to initiate polymerization to heat the carbon dioxide.

Suitabl free-radical initiators are all free-radical d nors which have a half-life of <3 hours at the temperatures selected. If, for example, polymerization is started at a low temperature and completed at a higher temperature, two or more initiators have to be used. By way of example, the following initiators are suitable at the stated polymerization temperatures:

50° to 60°C:

acetylcyclohexanesulfonyl peroxide, diacetyl peroxydicarbonate, dicyclohexyl peroxydicarbonate, di-2-ethylhexyl peroxydicarbonate, tert.-butyl perneodecanoate and 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile),

70° to 80°C:

tert.-butyl perpivalate, dioctanoyl peroxide, dilauroyl peroxide and 2,2'-azobis(2,4-dimethylvaleronitrile), tert.-butylazo-2-cyanobutane,

90° to 100°C:

dibenzoyl peroxide, tert.-butyl per-2-ethylhexanoate, tert.-butyl permaleate and 2,2-azobis(isobutyronitrile),

110° to 120°:

bis(tert.-butylperoxy)cyclohexane, tert.-butyl peroxyisopropylcarbonate and tert.-butyl peracetate,

130° to 140°C:

2,2-bis(tert.-butylperoxy)butane, dicumyl peroxide, ditert.-amyl peroxide and di-tert.-butyl peroxide,

150°:

p-menthane hydroperoxide, pinane hydroperoxide, cumene hydroperoxide and tert.-butyl hydroperoxide.

By concomitantly using redox coinitiators, for example benzoin, dimethylaniline or complexes or salts, which are soluble in organic solvents of heavy metals, such as copper, cobalt, manganese, iron, nickel or chromium, the half-lives of the stated peroxides, particularly the hydroperoxides, can be reduced, so that, for example, tert.-butyl hydroperoxide in the presence of 5 ppm of copper(II) acetylacetonate is effective at as low as 100°C.

Polymerization may be carried out in the presence of from about 0.05 to 10 percent, preferably about 0.1 to 5 percent by weight of polymerization regulators. Examples f suitable regulators are 2-mercaptoethanol, mercaptopropanols, mercaptobutanols, n-dodecylmercaptan, tert,-dodecylmercaptan, thioglycolic acid and thiophenol.

The reaction is generally carried out in a pressure vessel and since the reaction is exothermic the temperature is subsequently controlled by cooling. Excessively high temperatures may result in some degree of decomposition and crosslinking, rendering the polymer

insoluble in solvents. Acc rdingly, it is pref rr d to contr l the temperature at a maximum of 140°C and preferably a maximum of 85°C and in general the pressure should not exceed 4500 psi.

It is preferred that the reaction composition contain from about 1 to 50 percent carboxylic acid, about 50 to 95 percent CO_2, and about 0.1 to 0.7 percent initiator. It is most preferred that the composition contain about 10 to about 40 percent carboxylic acid: about 60 to about 90 percent carbon dioxide and about 0.1 to about 0.3 percent initiator.

For batch processing the reaction may be carri d out in any reactor capable of sustaining high pressures which is provided with adequate heating and cooling means. However, continuous processing methods are also possible. A continuous process is illustrated in the drawing which is a schematic view of one continuous process embodying the principles of the invention.

With reference more particularly to the drawing carbon dioxide is introduced into reactor 1 through conduit 3. Acrylic acid is metered into conduit 3 through conduit 5 and initiator is metered into conduit 3 through conduit 7. Pressure is maintained in conduit 3 and reactor 1 by means of carbon dioxide compressor 9. The reactor 1 may simply be a length of pipe with internal baffling to provide for

mixing f the reactants. The temperature in the react r is controlled by means of a jacket 11 supplied with heating and cooling fluids through conduit 13 which fluid exits through conduit 15. In order to initiate polymerization, the reaction mixture is heated in the reactor 1 by means of a hot fluid passing through the jacket 11. As the reaction proceeds it becomes exothermic and then it is necessary to cool the reaction by means of the fluid passing through jacket 11.

One means for accomplishing heating and cooling is to employ water as the cooling fluid entering through a conduit 17. One means for providing the necessary initial heat, is by injecting steam into the water in conduit 17 from a conduit 19 by means of a steam injection device 21. After the reaction becomes exothermic and self sustaining, little or no steam may be required since the primary purpose of the fluid in the jacket at this time is to maintain the reaction mass at optimum temperature. All this may be accomplished by means of a main control valve 23 and a steam control valve 25 which are controlled by a controller 27 connected to valves 23 and 25 by suitable means such as pneumatic or electrical connections 29 and 31. The controller 27 in turn is actuated by a temperature sensitive device (not shown) in the exit conduit 33 from the reactor 1 which temperature sensitive device is connected to the

c ntroll r 27 by suitabl means, i.e., el ctrical, pneumatic, etc., 35.

The product is continuously removed from the reactor 1 to one or more storage vessels through conduit 33. To permit continuous operation of the reactor 1, it is desirable to employ multiple storage tanks, for example three storage tanks 37, 39, and 41, provided with conduits 43, 45, and 47 respectively connected to conduit 33 through valves 49, 51, and 53. The product is continuously remov d from the reactor to the storage vessels where the pressure is reduced to atmospheric. At atmospheric pressure the CO_2 vaporizes leaving behind solid product. Accordingly, the multiple storage tanks 37, 39, and 41 are equipped with conduits 43, 45, and 47 and valves 49, 51, and 53 whereby the storage tanks may be used in rotation. Thus product can be transferred into one of the tanks, for example tank 37, with valve 49 open while valves 51 and 53 are closed to permit removal of the solid product from the other two tanks. The tanks are then used in rotation. Thus there is always a tank available to receive the product. Spray nozzles 50, 52 and 54 are provided in the tanks and the design of the spray nozzles can be such as to obtain a specific particle size of the polyacrylic acid product. The spray nozzle itself may act as a pressure reducing device whereby pressure in excess of 335 psi is maintained in the

reactor 1 and the conduits 33, 43, 45, and 47 on the supply side of the nozzles while the pressure is atmospheric in th tanks 37, 39, and 41. If the nozzles do not provide sufficient resistance to maintain the desired pressure in the reactor 1, a suitable conventional pressure reducing valve (not shown) may be provided in conduit 33 or three of them may be provided in conduits 43, 45, and 47, all as well known to those skilled in the art.

The carbon dioxide vapor returns to the system from the tanks through conduits 55, 57, and 59 and valves 61, 63, and 65 into conduit 67 to compressor 9 where it is compressed. The compressed carbon dioxide then passes through conduit 71 into supply conduit 3. Make up carbon dioxide and catalyst are added to the system as needed through valve 73.

The homopolymers of ethylenically unsaturated C_3- to C_5-carboxylic acids have many uses, for example, sizing agents in the textile industry, auxiliaries in the paper industry for improving the dry-strength of paper and as ingredients in detergents.

Unless otherwise stated, throughout the instant specification and claims, all temperatures are in °C and all percentages are by weight.

The following examples are provided in order to better illustrate the instant invention.

Th mol cular weight giv n in the Examples was measur d by g l permeati n chromatography (GPC) with aqu us elution agents. The separating columns were calibrated with polystyrene sulphonates having a narrow molecular weight distribution and supplied by Pressure Chem. Co., and the calibration was converted to the molecular weight of sodium polyacrylate on the BENOIT principle (J. Chim. Phys. <u>63</u> (1966) 1507) with the aid of the SPATORICO and BEYER measuring data (J. Appl. Polym. Sci. 19 (1975) 2933).

Examples 1-3

In each of the three examples, the amount of carbon dioxide in grams shown in the table below was charged to a 300-milliliter stainless steel autoclave equipped with an agitator, cooling coil, and electrical heating means. The CO_2 was then heated to the reaction temperature indicated in the table in °C which resulted in the respective reactor pressures set forth in the table. Acrylic acid in the amounts in grams shown in the Table along with a liquid initiator, also in the amounts in grams shown in the Table, were then charged and the tertiary mixture allowed to react. The initiator employed was Luazo* 82 2-t-butylazo-2-cyanobutane. Due to the exothermic condition, temperature and pressure increased to the values shown in the Table below. After reacting for 3 hours, the vessel was vented to remove the CO_2 and the pressure in the reaction vessel was reduced to atmospheric leaving a solid, water-soluble acrylic acid polymer having a molecular weight of about 10,000.

TABLE

Example No.	CO_2 (g)	Acrylic Acid (g)	Initiator (g)	Reaction Temp. (°C)	Exotherm Temp. (°C)	Reactor Press. (atm)	Exotherm Press. (atm)
1	125	52.0	1.25	80	146	117	205
2	155	20.6	0.50	80	83	205	270
3	160	10.0	0.20	78	83	290	300

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It will be n ted that the exotherm temperature f r Example 1 exceeded the maximum set forth above. The product also showed some slight signs of deterioration in Example 1. Accordingly, the exotherm temperature was controlled more carefully for Examples 2 and 3 through the use of the cooling coil, as shown in the Table above.

Example 4

Example 2 is repeated employing the continuous process and apparatus shown in the attached drawing and, described above. A solid, water-soluble acrylic acid polymer powder having a molecular weight of about 10,000 is produced.

Example 5

Thirty grams of acrylic acid, 0.3 g of tertiary-butyl-per-2-ethylhexanoate and 120 g of liquid carbon dioxide were placed in a 300 ml autoclave equipped with a stirrer and electrical heating means. The autoclave was then sealed, the contents were stirred and heated to a temperature of 80°C. The polymerization was carried out at 80°C for five hours. A pressure of 140 bar was measured under the reaction conditions. The pressure was then released and a fine powder of a water-soluble polyacrylic acid having a molecular weight of 500,000 was obtained. The polyacrylic acid can be used as an agent for improving the dry strength of paper.

Example 6

Exampl 5 was r peat d, exc pt that the polymerization was carried out at 90°C. A pressure of 185 bar was measured and a water-soluble polyacrylic acid having a molecular weight of 550,000 in the form of a fine powder was obtained.

Example 7

Thirty grams of acrylic acid, 0.9 g of tertiary-butyl perbenzoate, 0.1 g of 2-mercaptoethanol and 300 g of liquid carbon dioxide were placed in a 300 ml autoclave equipped with a stirrer and electrical heating means which was then sealed. The contents of the autoclave were then stirred and heated to a temperature of 120°C. This temperature was kept constant for five hours, the pressure being 230 bar. Thereafter the pressure in the autoclave was reduced to atmospheric, leaving a solid, water-soluble polyacrylic acid having a molecular weight of 100,000.

The polymer can be used in detergents as a substitute for sodium tripolyphosphate.

Example 8

Fifteen grams of methacrylic acid, 0.15 g of tertiary-butyl per-2-ethyl-hexanoate and 135 g of liquid carbon dioxide were placed in a 300 ml autoclave equipped with a stirrer and electrical heating means which was then sealed. The contents of the autoclave were stirred and

heated at 80°C and kept at the temperature for five h urs, the pressure being 160 bar. The pressure was then released. A fine powder of water-soluble polymethacrylic acid having a molecular weight of 100,000 was obtained. The polymer can be used in detergents as a substitute for sodium tripolyphosphate.

Example 9

Eight hundred grams of liquid carbon dioxide were introduced into a 2.5 liter autoclave equipped with a stirrer, a device for adding liquids and electrical heating means, and the autoclave was sealed. The contents of the autoclave were then heated at 80°C. As soon as this temperature was reached, a solution of 2 grams of tertiary-butyl per-2-ethylhexanoate in 200 g of acrylic acid was then continuously added to the autoclave over a period of 2.25 hours, the temperature being kept constant at 80°C and the pressure being 110 bar. After the addition of the monomer and the initiator, the reaction mixture was kept for two hours at 80°C. The pressure was then released; a flaky white voluminous powder of polyacrylic acid having a molecular weight of 350,000 was obtained. The polymer was soluble in water and can be used as a sizing agent in the textile industry.

Example 10

The procedure of Example 9 was repeated, except that 700 g of liquid carbon dioxide, 300 g of acrylic acid and 3 g of tertiary-butyl per-2-ethylhexanoate were used, the pressure being 100 bars. Here again, a flaky white voluminous powder of polyacrylic acid was obtained. The molecular weight of the polymer was 400,000.

The polymer obtained was water-soluble and can be used as an auxiliary in the production of dry-strength paper.

Example 11

The procedure of Example 10 was repeated, except that 450 g of carbon dioxide were used and the addition of acrylic acid and initiator was completed within two hours, the pressure being 85 bars. A lumpy water-soluble powder f polyacrylic acid having a molecular weight of 350,000 was obtained.

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The embodiments of the invention in which an exclusive privilege or property is claimed are defined as follows:

1. A process for preparing homopolymers of monoethylenically unsaturated C_3-C_5 carboxylic acids by polymerization of said acids in a polymerization zone in carbon dioxide in the presence of an initiator, wherein said polymerization is carried out at a temperature and pressure at which said carbon dioxide is in a supercritical state.

2. The process of claim 1, wherein th polymerization is carried out in a batch reactor.

3. The process of claim 1, wherein the polymerization is carried out in a continuous flow reactor.

4. The process of claim 1, 2 ou 3, wherein said initiator is 2-t-butylazo-2-cyanobutane.

5. The process of claim 1, 2 ou 3, wherein a polymerization regulator is also present.

6. The process of claim 1, wherein the polymerization is carried out with from about 1 to about 50 percent carboxylic acid, about 50 to about 95 percent carbon dioxide, and about 0.1 to about 0.7 percent initiator.

7. The process of claim 6, wherein a polymerization regulator is also present in an amount of about 0.05 to about 10 percent.

8. The process of claim 1, wherein th polymerization is carried out with about 10 to about 40

percent carboxylic acid, about 60 to about 90 percent carbon dioxide, and 0.10 to 0.3 percent initiator.

9. The process of claim 8, wherein said initiator is 2-t-butylazo-2-cyanobutane.

10. The process of claim 8, wherein said initiator is tertiary-butyl per-2-ethylhexanoate.

11. The process of claim 8, 9 or 10, wherein a polymerization regulator is also present in an amount of about 0.1 to 5.0 percent.

12. The process of claim 6, wherein the polymerization temperature is about 31 to 140°C, the polymerization pressure is about 1070 to 4500 psi, and the polymerization time is about 0.25 to 5 hours.

13. The process of claim 12, wherein the polymerization temperature is about 31 to 85°C.

14. The process of claim 6, 12 or 13, wherein said initiator is 2-t-butylazo-2-cyanobutane.

15. The process of claim 6, 12 or 13, wherein said initiator is tertiary-butyl per-2-ethylhexanoate.

16. The process of claim 6, ~~12~~ or 13, wherein the carboxylic acid polymer has a molecular weight of from about 1,000 to 1,000,000.

17. The process of claim 12, wherein the carboxylic acid polymer has a molecular weight of from about 1,000 to 1,000,000.

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18. The process of claim 6, 12 or 17, wherein the polymerization is carried out in a batch reactor.

19. The process of claim 6, 12 or 17, wherein the polymerization is carried out in a continuous flow reactor.

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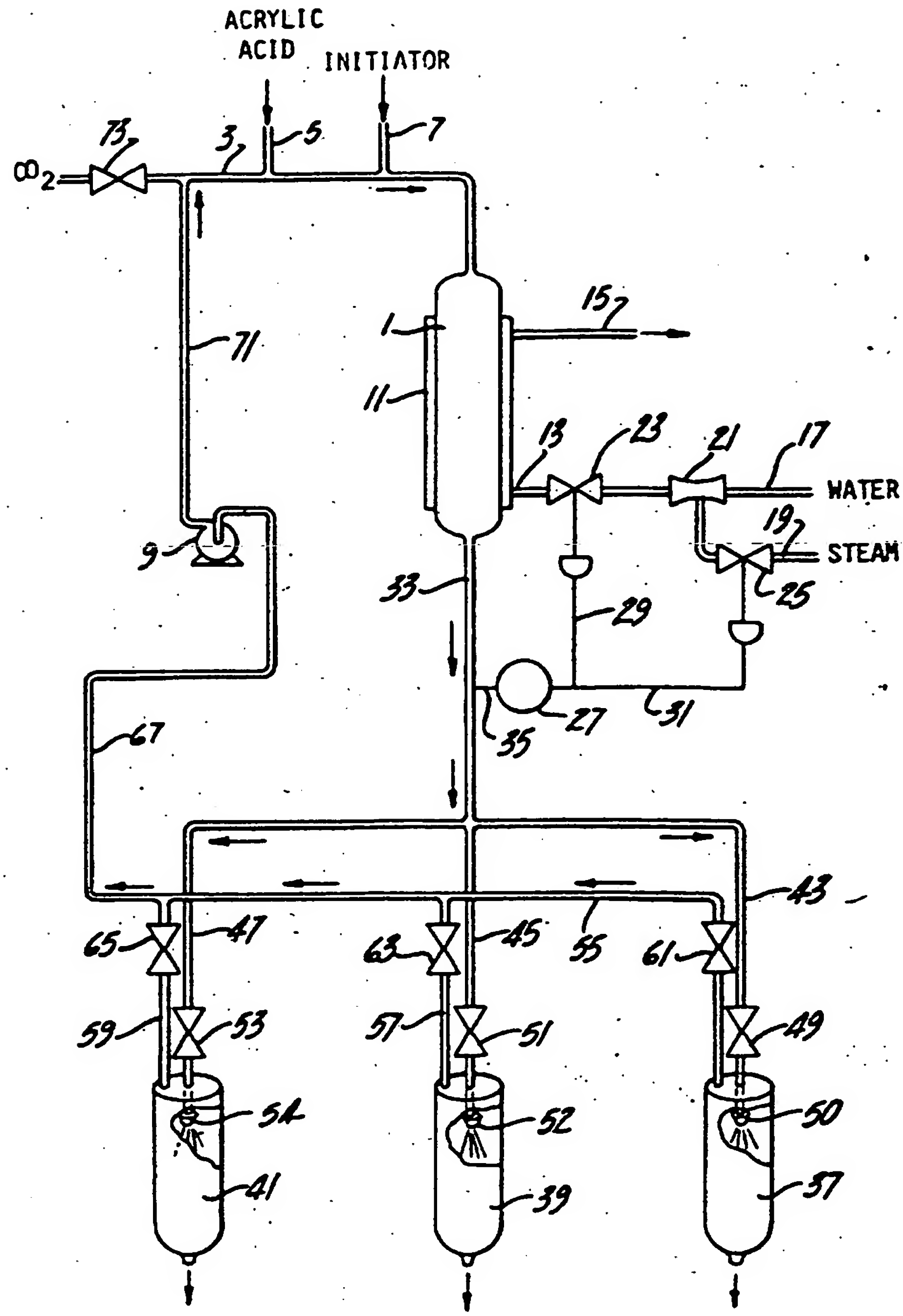
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ACID
INITIATOR
CO2
WATER
STEAM
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